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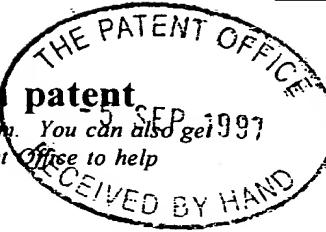
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Dated 24 September 1998

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CAMBRIDGE DISPLAY TECHNOLOGY LIMITED  
13 STATION ROAD,  
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Patents ADP number (*if you know it*)

6166441001

If the applicant is a corporate body, give the  
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4. Title of the invention

SELF-ASSEMBLED TRANSPORT LAYERS FOR OLEDs

5. Name of your agent (*if you have one*)

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## SELF-ASSEMBLED TRANSPORT LAYERS FOR OLEDs

The present invention relates to an improved fabrication process for organic light-emitting devices, and a structure formed thereby.

Organic light-emitting devices (OLEDs) such as described in earlier US patent No. 5,247,190 assigned to Cambridge Display Technology Limited, or in Van Slyke et al., US Patent No. 4,539,507, the contents of which are herein incorporated by reference and example, have great potential for use in various display applications, such as large-area flat-panel displays. Principally, an OLED consists of an anode that injects positive charge carriers, a cathode that injects negative charge carriers and at least one organic electroluminescent layer sandwiched between the two electrodes. Under application of a positive bias to the anode, holes are injected from the anode and electrons from the cathode. These carriers recombine within the organic electroluminescent layer, giving out light.

Typically, although not necessarily, the anode is a thin film of, for example, indium-tin-oxide (ITO), which is a semi-transparent conductive oxide which is commercially readily available already deposited on glass or plastic substrates. The organic layer(s), typically a thin (100 - 1000 nm) layer of conjugated polymer, is normally deposited onto the ITO-coated substrate by, for example, evaporation, or any one of spin-coating, blade-coating, dip-coating or meniscus-coating. The final step of depositing the cathode layer, typically a low work-function metal electrode, onto the organic layer is normally performed by thermal evaporation or sputtering of a suitable cathode metal. Layers of Al, Ca or alloys of Mg:Ag or Mg:In or Al alloys are often used as cathode materials.

One of the key advantages of the OLED technology is that devices can be operated at low drive voltages, provided that suitable electro-luminescent organic layers, and electrodes with good

efficiencies for the injection of positive and negative charge carriers, are used.

Key performance parameters for the performance of a polymer LED are the quantum efficiency (the number of emitted photons per charge carrier flowing in the circuit), and the drive voltage required to achieve a given light output. Another important parameter is the power efficiency (the ratio of optical power output to electrical power input). High power efficiency requires both high quantum efficiency and low drive voltage. Further important parameters in polymer LEDs are the maximum brightness achievable, the ease and reproducibility of manufacture, and the operating lifetime.

In order to achieve good performance in OLEDs it is of great importance to optimise all individual layers, the anode, the cathode and the organic layer(s), as well as the interfaces between the layers.

The provision of a thin, very well defined polymer layer between either one of the cathode or anode and the organic layer, a so-called interfacial layer, can improve device performance. However, it is essential to achieve the improved performance that such layer is fabricated under extremely well controlled conditions. Controlling the thickness in the nanometre regime is important to optimise the device performance.

A technique known as self-assembly can be used to build a well defined polymer layer. The technique of polymer self-assembly comprises building up a polymer film by adsorption of successive polymer layers from solution. The technique relies on attractive interaction between successive layers, and requires that each layer formed is dissimilar to the previous layer formed. Typically a repeating sequence of polymer layers may be used, such as ABAB ... , or ABCDABCD ... , where A, B, C, and D denote respective dissimilar layers.

Polymer light emitting devices fabricated using a self-assembly process are described

in, A. C. Fou, O. Onitsuka, M. Ferreira and M. F. Rubner, "Interlayer interactions in self-assembled poly(phenylenevinylene) multilayer heterostructures: implications for light-emitting and photorectifying diodes," Mat. Res. Soc. Symp. Proc., Vol. 369, pp. 575-580, 1995; and A. C. Fou, O. Onitsuka, M. Ferreira, M. F. Rubner and B. R. Hsieh, "Fabrication and properties of light-emitting diodes based on self-assembled multilayers of poly(phenylene vinylene)," J. Appl. Phys., Vol. 79, pp. 7501-7509, 1996.

In these references a technique of self-assembly is utilised using polycations and polyanions described in G. Decher, J. D. Hong and J. Schmitt, "Buildup of ultrathin multilayer films by a self-assembly process. 3. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces," Thin Solid Films, Vol. 210, pp. 831-835, 1992. In these structures PPV precursor or its derivatives are used as the polycation, with various polyanions such as polystyrenesulfonate or sulphinated polyaniline. Poly(*p*-pyridylvinylene) and its derivatives have also been used to make self-assembled LEDs.

The process of producing by self-assembly a film of sufficient thickness to give a working LED is extremely time-consuming, due to the number of dipping and rinsing steps involved. In the work described above, the entire device was completed by self-assembly, thus retaining the problem of many dipping steps. This method is unlikely to be commercially viable.

It is therefore an object of the present invention to provide a structure, and fabrication process, in which a well-defined, thin, polymer interfacial layer may be provided between an electrode and the electroluminescent material of an OLED without unduly inhibiting the standard commercial fabrication process.

Thus, according to a first aspect of the present invention there

is provided a method of fabricating an organic light-emitting device, comprising the steps of: forming a first electrode for the device over a substrate; forming, by self-assembly, at least one polymer layer over the first electrode; forming, other than by self-assembly, at least one layer of organic light emissive material over the at least one polymer layer; and forming a second electrode for the device over the at least one layer of organic light emissive material.

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This first aspect of the present invention also provides a method of fabricating an organic light-emitting device, comprising the steps of: forming a first electrode for the device over a substrate; forming, other than by self-assembly, at least one layer of organic light emissive material over the first electrode; forming, by self-assembly, at least one polymer layer over the at least one layer of organic light emissive material; and forming a second electrode for the device over the at least one polymer layer.

Thus in the first aspect of the present invention, self-assembly has been used to form at least one layer of additional polymer at an electrode/light-emissive layer interface. The rest of the device is then completed using standard techniques such as spin-coating. This first aspect of the present invention has the benefits of rapid processing, with the enhancements of well-controlled layers at the polymer interface.

Thus the first aspect of the present invention gives a reduction in processing time and cost compared with prior art devices fabricated entirely by self-assembly

Significant improvement in quantum efficiency, drive voltage, power efficiency and/or maximum luminance compared with devices without the interfacial layer are obtained, as well as improvements in device lifetime.

Quantum efficiency is significantly enhanced over a range of

interfacial layer thicknesses, whereas the drive voltage begins to increase with the thicker layers. An optimum power efficiency therefore occurs at an intermediate thickness. This thickness is smaller than can typically be achieved with spin-coated interfacial layers. Self-assembly provides thin, continuous, well-defined films in this thickness regime. This is an ideal technique for producing pin-hole free films in this thickness regime.

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The at least one self-assembled polymer layer preferably comprises one or more pairs of cooperating sub-layers, and the at least one organic light emissive layer comprises a continuous layer having the same composition throughout.

The at least one self-assembled polymer layer may be any one of an insulating polymer, a semiconducting polymer, or a conducting polymer. Deposition, by self-assembly, of either insulating, semiconducting or conducting polymer interfacial layers in OLEDs allows further optimisation of device performance.

The pair of cooperating sub-layers interact by attractive forces, each sub-layer being dissimilar to the other. Preferably one sub-layer of the pair is positively charged and the other sub-layer of the pair is negatively charged.

Preferably the positively charged sub-layer of the pair is formed by immersing the substrate in a polycation electrolyte solution and the negatively charged sub-layer of the pair is formed by immersing the substrate in a polyanion solution.

If the polymer is an insulating polymer, the polyanion electrolyte solution preferably comprises the structure of Figure 2(a), and the polycation solution preferably comprises the structure of Figure 2(b).

If the polymer is a semiconducting polymer, the polyanion electrolyte solution preferably comprises the structure of Figure

2(c), and the polycation solution preferably comprises the structure of Figure 2(d).

If the polymer is a conducting polymer, the polyanion electrolyte solution preferably comprises the non-protonated form of the structure of Figure 2(e), and the polycation solution preferably comprises the structure of Figure 2(f).

The cooperating sub-layers may, in an alternative example, interact by acceptor/donor interaction. Preferably such acceptor/donor interaction is provided by hydrogen bonding.

Hydrogen bonding techniques in general are discussed, for example, in W.B. Stockton and M.F. Rubiner, "Molecular-Level Processing of Conjugated Polymers. 4. Layer-by-Layer Manipulation of Polyaniline via Hydrogen-Bonding Interactions", *Macromolecules*, 1997, 30, 2717-2725.

Preferably each sub-layer of the cooperating pairs of sub-layers is between 0.3 and 2nm thick, and preferably is 1 nm thick.

The at least one polymer layer preferably comprises a plurality of pairs of sub-layers, for example two, four, or ten pairs.

The at least one polymer layer may alternatively comprise three or more cooperating sub-layers, each sub-layer being dissimilar to any other. The at least one polymer layer may comprise a plurality of the three or more sub-layers.

Preferably, the at least one polymer layer is between around 0.3 to 20nm thick.

The organic material may be either a conjugated polymer, or a low molecular weight compound. The at least one layer of organic material may comprise a composite structure including at least one layer of a conjugated polymer and at least one layer of a low molecular weight compound.

If the at least one layer of organic material is a polymer then it is preferably a semiconductive conjugated polymer. The semiconductive conjugated polymer is preferably PPV or a derivative thereof.

The at least one layer of organic light-emissive material may be formed by any one of spin-coating, blade-coating, meniscus-coating, or dip-coating,

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The at least one layer of organic material preferably has a thickness in a range of about 30nm to 1000nm, and preferably of about 90nm.

The method may further comprise the step of, prior to the step of forming the at least one polymer layer, removing physisorbed water from the surface of the substrate. The step of removing the physisorbed water from the surface preferably comprises heating the substrate.

The method may further comprise the step of, prior to the step of forming the at least one polymer layer, forming a coupling layer. The step of forming the coupling layer preferably comprises silylating the substrate. If the step of removing the physisorbed water is performed, then the step of forming the coupling layer is performed thereafter.

The substrate may have a pH dependent surface charge, and the method may further comprise preparing the surface of the substrate prior to self-assembly by making the surface charge pH independent.

The method may further comprise preparing the surface of the substrate prior to self-assembly, wherein the surface comprises amino groups, the method comprising the step of quaternising the amino groups. The quaternised surface is positively charged.

The method may further comprise preparing the surface of the

substrate prior to self-assembly, wherein the surface comprises thiol groups, the method comprising the step of oxidising the thiol groups. The oxidised surface is negatively charged.

The starting substrate, prior to formation of the first electrode, may comprise one of a glass or plastic material. The substrate may comprise any one of polyester, polycarbonate, polyimide, or poly-ether-imide.

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The method may further comprise the step of forming a layer of conductive material over the second electrode. The conductive material preferably comprises aluminium or an alloy thereof. The conductive material may be sputter deposited, preferably by DC magnetron or RF sputtering, or evaporated, preferably by resistive or electron-beam thermal evaporation.

The first electrode may be a cathode and the second electrode an anode, or the first electrode may be an anode and the second electrode a cathode.

The cathode may comprise a light-transmissive conductive oxide, preferably indium-tin-oxide, tin oxide, or zinc oxide. The cathode may be sputter deposited or evaporated.

The anode may comprise a light-transmissive conductive oxide, preferably indium-tin-oxide, tin oxide, or zinc oxide. The anode may be sputter deposited or evaporated.

The first aspect of the present invention also provides an organic light-emitting device comprising: at least one layer of organic light-emissive material between a first electrode and a second electrode, the at least one organic light-emissive material having been formed other than by self-assembly; and at least one polymer layer between one of the first and second electrodes and the at least one organic light-emissive material, the at least one polymer layer being formed by self-assembly.

Preferably, the at least one polymer layer comprises at least one pair of cooperating sub-layers, and the at least one layer of organic material is a continuous layer having a consistent composition throughout.

The at least one polymer layer preferably comprises a plurality of pairs of cooperating layers.

In a preferential embodiment of the present invention the technique of self-assembly of polyelectrolytes is used to deposit thin, well-defined layers of insulating, semiconducting, or conducting polymers between a - preferably ITO - electrode and an emissive polymer in polymer LEDs. In this technique, a substrate is dipped alternately into polycation and polyanion solutions, depositing alternate layers by electrostatic attraction. The self-assembly technique deposits only a thin interfacial layer; the rest of the device is deposited, preferably, by spin coating. This gives a significant reduction in processing time compared with prior art devices made entirely by self- assembly.

Since each self-assembled layer is thin and contiguous, well-defined structures can be built up in accordance with this aspect of the present invention with control of thickness of the interfacial layer in the nanometre regime. The present invention also provides the optimum materials and thickness for these interfacial layers in order to optimise the quantum and power efficiencies of polymer LEDs. Significantly enhanced power efficiencies and significantly enhanced maximum brightnesses are achieved by the use of the present invention.

The self-assembly process preferably requires a starting surface with a well-defined surface charge. This is typically achieved by forming a coupling layer on the surface prior to self-assembly, typically by surface treatment with a silylating agent.

It is a second object of the present invention to provide an improved starting surface for a self-assembly process in fabricating an organic LED, or a part thereof.

In a second aspect of the present invention there is provided a method of fabricating an organic light-emitting device, comprising the steps of: forming a first electrode for the device over a substrate; removing physisorbed water from the surface of the first electrode; forming a coupling layer; forming, by self-assembly, at least one polymer layer over the first electrode; forming at least one layer of organic light emissive material over the at least one polymer layer; and forming a second electrode for the device over the at least one layer of light emissive material.

The step of forming this coupling layer preferably comprises silylating the substrate.

The second aspect of the present invention also provides a method of fabricating an organic light-emitting device, comprising the steps of: forming a first electrode for the device over a substrate; forming at least one layer of organic light emissive material over the first electrode; removing physisorbed water from the surface of the at least one organic light-emissive material; forming a coupling layer; forming, by self-assembly, at least one polymer layer over the at least one layer of light emissive material; and forming a second electrode for the device over the at least one polymer layer.

The removal of physisorbed water, preferably by heating of the ITO substrate in vacuum, from the surface prior to surface silylation and LED production, results in the production of a well-defined surface prior to self-assembly, and consequently improved control of interfacial layer quality. This second aspect of the invention also provides a reduction in device degradation by removal of water close to the interfacial layer. Without the removal of the physisorbed water, the coupling layer may form a

gel when deposited, floating on the surface. Thus this second aspect of the invention provides an improvement in the bonding of the coupling layer to the electrode.

It is a third object of the present invention to provide an improved starting surface for a self-assembly process, such that the implementation of the self-assembly process is versatile.

According to a third aspect of the present invention there is provided a method of preparing a surface having a pH dependent surface charge prior to self-assembly comprising the step of making the surface charge pH independent. The surface is preferably of a substrate of a light-emitting device. The light-emitting device is preferably an organic light-emitting device.

The third aspect of the present invention also provides a method of preparing a surface comprising amino groups prior to self-assembly comprising the step of quaternising the amino groups. The surface is preferably of a substrate of a light-emitting device. The light-emitting device is preferably an organic light-emitting device. The quaternised surface is positively charged.

The third aspect of the present invention further provides a method of preparing a surface comprising thiol groups prior to self-assembly comprising the step of oxidising the thiol groups. The surface is preferably of a substrate of a light-emitting device. The light-emitting device is preferably an organic light-emitting device. The oxidised surface is negatively charged. After oxidation, the surface is preferably deprotonated with an alkali.

Many polyions are only stable at certain pH values, so the quaternisation and oxidation steps respectively allow a wider range of polyions to be deposited in LED structures than was previously possible without changing the coupling agent. This allows a range of polycations and polyanions (which require different pH values to be stable as ions in solution) to be self-

assembled using the same coupling agent.

Quaternisation and oxidation techniques are described, for example, in J. March, "Advanced Organic Chemistry:Reactions, Mechanisms and Structure", 3rd Ed., John Wiley & Sons, New York, 1985, Chapters 10 and 19.

As a result of either the quaternisation or the oxidation processes according to the third aspect of the invention, the resultant coupling agents advantageously have greatly reduced susceptibility to oxidation, a process which can be a problem in devices.

The invention will now be described with reference to the accompanying drawings in which:

Figure 1 illustrates an OLED fabricated in accordance with the present invention;

Figure 2 illustrates examples of the composition of particular layers of the structure of Figure 1;

Figure 3 illustrates the efficiency obtained by described examples of devices according to the present invention;

Figure 4 illustrates the power efficiency obtained by described examples of devices according to the present invention;

Figure 5 illustrates the luminance obtained by described examples of devices according to the present invention;

In a first example, a device is fabricated on a commercial 1x1 cm<sup>2</sup> ITO (indium-tin-oxide)-glass substrate (Balzers). Referring to Figure 1, such an exemplary substrate is shown in which an ITO layer 4 is formed on a glass substrate 2. For all chemical treatment steps in this first example, the substrate is held in a vertical configuration on PTFE substrate-holders. The solvents

used in this example are of HPLC grade or better, unless otherwise noted. Reagents used are of AR grade or better.

In a first step, the ITO layer is patterned and cleaned. The ITO surface is selectively coated with a commercial photoresist and then baked at 45°C for 10 minutes in an oven. The exposed areas are etched off in 200 mL 5 wt% HCl at 60-65 °C for 45 min. The photoresist is then stripped off in 2x100 mL acetone.

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The patterned ITO substrate is then cleaned using an RCA recipe (10:2:0.6 H<sub>2</sub>O-H<sub>2</sub>O<sub>2</sub>-NH<sub>3</sub>, 200 mL), mildly-agitated at 55-60 °C, for 75 minutes.

In a second step a coupling layer, shown in Figure 1 as a layer 6, is formed in preparation for the layer-by-layer self-assembly. Preferably and advantageously, the substrate is heated in a dynamic vacuum to 165-170 °C for 2 - 3 hours in a vacuum oven to remove physisorbed H<sub>2</sub>O prior to surface silylation.

The substrate is then cooled in air briefly to 100 °C, and then immersed in a 200-mL toluene bath containing 5 vol% 3-aminopropyltrimethoxysilane. The reaction bath was warmed to 95-97 °C for 2 hours, taking care to exclude moisture. This gives an ITO surface functionalised with amino (-NH<sub>2</sub>) groups tethered to the end of a short C<sub>3</sub> alkyl chain.

The silylated substrates are washed in 2x100 mL toluene and 1x MeOH in that order, and dried under a jet of N<sub>2</sub>. Visual inspection of the specular reflection off the ITO surface at this point shows an optically-clear, homogenous surface with very few scattering particles on a pinhole-free ITO film.

The amino groups are then preferably, and advantageously, quaternised to the pH-insensitive trimethylammonium (-NMe<sub>3</sub><sup>+</sup>) moiety, and to achieve this the substrate is immersed in 200mL N,N-dimethylformamide containing 5 vol% CH<sub>3</sub>I and 0.6 vol% Et<sub>3</sub>N for 3 hours. The reaction bath is kept in the dark at room

temperature (24 °C).

The quaternised substrate is washed in 2x100 mL MeOH, 1x100 mL 0.45- $\mu$ m filtered H<sub>2</sub>O, and then 1x100 mL 0.45- $\mu$ m filtered IPA in that order and blown dry in a jet of N<sub>2</sub>. Visual inspection at this point shows the surface to remain optically-clear and homogenous.

In a third step the interfacial layer, denoted in Figure 1 by layer 8, is constructed using layer-by-layer self-assembly.

The self-assembly fabrication steps may be performed by any number of self-assembly techniques. In one alternative the attractive forces by which the pairs of cooperating sub-layers interact is provided by an acceptor/donor interaction, and specifically by hydrogen bonding.

In the preferred technique used in relation to the examples described herein, the attractive forces by which the pairs of cooperating sub-layers interact is provided using oppositely charged layers for respective ones of the sub-layers of each pair.

In the first example, the layer-by-layer self-assembly third step is performed on the derivatised ITO-substrates in a laminar flow cabinet at room temperature.

Each assembly cycle assembles a bilayer, that is a pair of cooperating sub-layers, and consists of the following steps:

- (i) Immersion in a polyanion electrolyte bath (static) for 14 min;
- (ii) Rinsing in a fresh H<sub>2</sub>O (Millipore) bath (mildly-agitated) for 10 s;
- (iii) Immersion in a polycation bath (static) for 14 min;
- (iv) Rinsing in a fresh H<sub>2</sub>O (Millipore) bath (mildly-agitated) for 10 s.

The assembled films are preferably not allowed to dry out between sequential steps. Carryover and cross-contamination of solutions were minimised by careful handling and rinsing.

The polyanion electrolyte bath, in this example where the interfacial layer is an insulating polymer, contains 20 mL H<sub>2</sub>O (Millipore), 21 mg of poly(styrene sulfonic acid, Na salt) (Aldrich, MW 70k), 30 mg NaCl and aq HCl to adjust the pH to ca.

3. The polycation bath, in this example in which the interfacial layer is an insulating polymer, contains 20 mL H<sub>2</sub>O (Millipore), 8 mg of poly(allylamine hydrochloride) (Aldrich, MW 50-65k), 30 mg NaCl and aq HCl to adjust the pH to ca. 3. After the self-assembly steps (i) to (iv), the bi-layer has one sub-layer of the structure of Figure 2(a), and one sub-layer of the structure of Figure 2(b).

In a first exemplification of this first example the steps (i) to (iv) were performed twice to assemble a structure having two bilayers, or two pairs of sub-layers.

The substrate is then rinsed in 2x40 mL H<sub>2</sub>O (Millipore) for 2 minutes. The substrate is then dried under dynamic vacuum for 5 hours.

The quaternisation step of the third step is advantageous since it results in a positively charged surface, such that the surface may then be immersed in either a basic solution or an acid solution during self-assembly. Quaternisation makes the surface charge of such a described device pH independent, thereby enabling use of the basic or acid solution.

In an alternative, the ITO surface is functionalised with thiol groups, and a different step is needed to make such surface pH independent. In this alternative, in the second step the coupling layer, shown in Figure 1 as the layer 6, is again formed in preparation for the layer-by-layer self-assembly. The substrate is again heated in a dynamic vacuum to 165-170 °C for

2 - 3 hours in a vacuum oven to remove physisorbed H<sub>2</sub>O prior to surface silylation.

The substrate is then again cooled in air briefly to 100 °C, and then immersed in a 200-mL toluene bath containing 5 vol% 3-mercaptopropyltrimethoxysilane. The reaction bath was warmed to 95-97 °C for 2 hours, taking care to exclude moisture. This gives an ITO surface functionalised with thiol (-SH) groups tethered to the end of a short C<sub>3</sub> alkyl chain.

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The silylated substrates are washed in 2x100 mL toluene and 1x MeOH in that order, and dried under a jet of N<sub>2</sub>. Visual inspection of the specular reflection off the ITO surface at this point shows an optically-clear, homogenous surface with very few scattering particles on a pinhole-free ITO film.

The thiol groups are then, in this alternative second step, preferably and advantageously oxidised to the pH-insensitive sulfonate (-SO<sub>3</sub>) moiety, and to achieve this the substrate is immersed in 200mL H<sub>2</sub>O containing 10 mL HCOOH and 30 mL H<sub>2</sub>O<sub>2</sub> for 30 minutes at room temperature (24°C).

The oxidised substrate is washed in 2x100 mL H<sub>2</sub>O, 1x100 mL dilute NaOH (0.02M), 2 x 100mL 0.45 µm-filtered H<sub>2</sub>O, and then 1x100 mL 0.45-µm filtered iso-propyl alcohol (IPA) in that order and blown dry in a jet of N<sub>2</sub>. Visual inspection at this point shows the surface to remain optically-clear and homogenous.

In this alternative further, the third step is varied, although the interfacial layer, denoted in Figure 1 by layer 8, is again constructed using layer-by-layer self-assembly of the interfacial layer. The assembly is performed on the derivatised ITO-substrates in a laminar flow cabinet at room temperature.

Each assembly cycle assembles a bilayer, that is a pair of cooperating sub-layer, and consists, in this alternative, of the following steps:

- (i) Immersion in a polycation bath (static) for 14 min;
- (ii) Rinsing in a fresh H<sub>2</sub>O (Millipore) bath (mildly-agitated) for 10 s;
- (iii) Immersion in a polyanion electrolyte bath (static) for 14 min;
- (iv) Rinsing in a fresh H<sub>2</sub>O (Millipore) bath (mildly-agitated) for 10 s.

The assembled films are preferably not allowed to dry out between sequential steps. Carryover and cross-contamination of solutions were minimised by careful handling and rinsing.

The polyanion electrolyte bath, in this alternative example where the interfacial layer is again an insulating polymer, again contains 20 mL H<sub>2</sub>O (Millipore), 21 mg of poly(styrene sulfonic acid, Na salt) (Aldrich, MW 70k), 30 mg NaCl and aq HCl to adjust the pH to ca. 3. The polycation bath, in this alternative example in which the interfacial layer is again an insulating polymer, again contains 20 mL H<sub>2</sub>O (Millipore), 8 mg of poly(allylamine hydrochloride) (Aldrich, MW 50-65k), 30 mg NaCl and aq HCl to adjust the pH to ca. 3. After the self-assembly steps (i) to (iv), the bi-layer again has one sub-layer of the structure of Figure 2(a), and one sub-layer of the structure of Figure 2(b).

In a fourth step an emissive MEH-PPV layer, shown in Figure 1 as layer 10, is spin coated onto the device. 90-nm of poly(2-methoxy, 5-(2'-ethyl)-hexyloxy-p-phenylenevinylene) [MEH-PPV] is deposited on the substrate-polymer assembly by spin-coating of a 0.5 wt% CHCl<sub>3</sub> solution of the MEH-PPV at 2000 rpm for 1 min.

In a fifth step, the thus far constructed device is thermally treated. The semi-completed device is baked at 100 °C for 1 hour under dynamic vacuum (P < 10<sup>-4</sup> mbar) to drive off free H<sub>2</sub>O. The substrates are then slowly cooled to 50 °C over 2 hours, still in vacuo .

A sixth step is a metal electrode deposition step. Without breaking vacuum, a 200-nm thick Ca layer is thermally evaporated at a base pressure of  $6 \times 10^{-6}$  mbar, through a mask, onto the MEH-PPV to give  $4.4 \text{ mm}^2$  devices. A 100-nm thick Al layer is then finally evaporated to protect the Ca electrode.

Thus, a first example of an OLED according to the present invention is completed. As a control, for comparison with the advantageous performance characteristics achieved by the examples described herein implementing the concepts of the present invention, MEH-PPV is also spun directly on RCA-cleaned ITO. Devices prepared from the RCA-cleaned ITO are designated as "conventional devices" hereafter.

For the device according to the first example with the insulating polymer interfacial layer, a maximum efficiency of 0.92 cd/A at 7V is obtained, compared with 0.16 cd/A at 7V for the conventional device, representing an improvement by a factor of 5.8. The device according to the first example with the insulating polymer interfacial layer has a current density of 170 mA/cm<sup>2</sup>, compared with 930 mA/cm<sup>2</sup> for the conventional device, representing a decrease by a factor of 5. The device according to the first example with the insulating polymer interfacial layer has a maximum power efficiency of 0.45 lm/W at 6V, compared with 0.079 lm/W at 7V for the conventional device, representing an increase by a factor of 5.8. The device according to the first example with the insulating polymer interfacial layer has a maximum luminance of 2100 cd/m<sup>2</sup> at 8V, compared with 1300 cd/m<sup>2</sup> at 7V for the conventional device, representing an increase by a factor of 1.6.

To illustrate the advantageous performance of an OLED assembled according to the present invention, reference is now made to Figures 3, 4, and 5. Figures 3, 4, and 5 illustrate experimental results achieved by devices assembled according to the present invention against those results achieved with conventional devices. Figures 3, 4, and 5 illustrate efficiency, power

efficiency, and luminance of the devices respectively.

A number of devices are fabricated as described in the first example, except that the number of bilayers deposited in the third step is varied. Devices with 1, 2, 4 and 10 bilayers, or pairs of sub-layers, were assembled by performing the step (i) to (iv) once, twice, four times and ten times respectively. In Figures 2 to 4, points IP-1, IP-2, IP-4 and IP-10 represent the results for a device assembled according to the first example with 1, 2, 4 and 10 bilayers respectively. These results demonstrate that the power efficiency is optimised with two bilayers of the insulating polymer illustrated in Figures 2 (a) and (b).

In a second example, devices are fabricated as described in the first example above, except that in the third step the polyanion bath contains 20 mL H<sub>2</sub>O (Millipore), 22 mg of poly(styrene sulfonic acid, Na salt) (Aldrich, MW 70k), 30 mg NaCl and aq HCl to adjust the pH to ca. 3; and the polycation bath contains 20 mL H<sub>2</sub>O (Millipore), 0.76 g of a 3.0 wt% MeOH solution of the tetrahydrothiophenium chloride precursor to poly(phenylene vinylene), 30 mg NaCl and aq HCl to adjust the pH to ca. 3. After the self-assembly steps (i) to (iv), the bi-layer again has one sub-layer of the structure of Figure 2(c), and one sub-layer of the structure of Figure 2(d). The fifth, thermal treatment step, is found to develop short conjugation lengths in the PPV-precursor polymer to give a semiconducting polymer.

For the device according to the second example with the semiconducting polymer interfacial layer, a maximum efficiency of 0.73 cd/A at 6.5V is obtained, representing an improvement by a factor of 4.6 compared with the conventional device. The device according to the second example with the semiconducting polymer interfacial layer has a current density of 970 mA/cm<sup>2</sup>, similar to the conventional device. The device according to the second example with the semiconducting polymer interfacial layer has a maximum power efficiency of 0.364 lm/W at 6V, representing

an increase by a factor of 4.6 compared with the conventional device. The device according to the second example with the semiconducting polymer interfacial layer has a maximum luminance of 7900 cd/m<sup>2</sup> at 7.5V, representing an increase by a factor of 6.0 compared with the conventional device.

In the second example a number of devices were fabricated as described in the first example above, except that the number of bilayers deposited in the third step was varied. Again, devices with 1, 2, 4 and 10 bilayers were formed. The values of efficiency, power efficiency and maximum luminance for these devices are shown in Figures 3, 4 and 5 respectively. In Figures 3 to 5, points SP-1, SP-2, SP-4 and SP-10 represent the results for a device assembled according to the second example for 1, 2, 4 and 10 bilayers respectively. These results demonstrate that the efficiency, power efficiency and maximum luminance are all optimised with two bilayers, or two pairs of sub-layers, of the semiconducting polymer of Figure 2(c) and (d).

In a third example a device is fabricated as described above in the first example, except that in the third step the polyanion bath contains 20 mL H<sub>2</sub>O (Millipore), 16 mg of sulfonated polyaniline, 30 mg NaCl and concentrated NH<sub>3</sub> to adjust the pH to ca. 11., and the polycation bath contains 20 mL H<sub>2</sub>O (Millipore), 17 mg of hexadimethrine bromide (Aldrich), 30 mg NaCl and concd NH<sub>3</sub> to adjust the pH to ca. 11. After deposition of the interfacial layer, the substrate is briefly immersed in a 0.2 M HCl solution to protonate the interfacial layer, giving the conducting form of polyaniline. Thus the third example assembles a structure in which the interfacial polymer layer is a conducting polymer, the bi-layer having one sub-layer of the structure of Figure 2(e), and one sub-layer of the structure of Figure 2(f).

The device assembled according to the third example with the conducting polymer interfacial layer has a maximum efficiency of 0.44 cd/A at 6.5V, representing an improvement by a factor of 2.8

compared with the conventional device. The device assembled according to the third example with the conducting polymer interfacial layer has a current density of  $1430 \text{ mA/cm}^2$ , representing an increase by a factor of 1.5 compared with the conventional device. The device assembled according to the third example with the conducting polymer interfacial layer has a maximum power efficiency of  $0.23 \text{ lm/W}$  at 6V, representing an increase by a factor of 3.0 compared with the conventional device. The device according to the third example with the conducting polymer interfacial layer has a maximum luminance of  $7300 \text{ cd/m}^2$  at 7V, representing an increase by a factor of 5.6 compared with the conventional device.

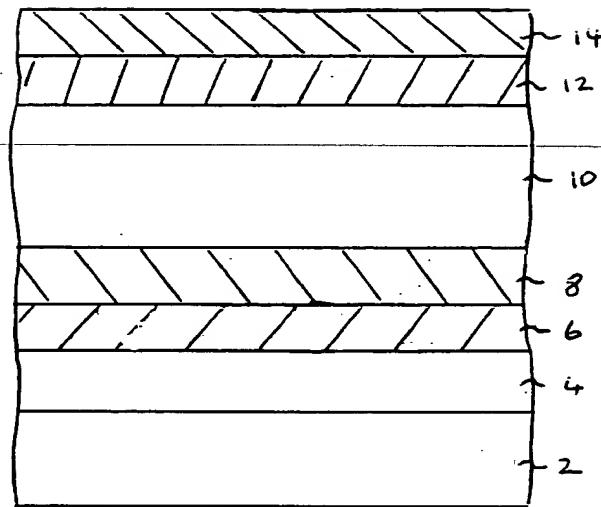
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A number of devices are fabricated as described in the first example, except that the number of bilayers deposited in the third step is again varied. Again, devices with 1, 2, 4 and 10 bilayers, or pairs of sub-layers, are used. In Figures 3 to 5, points CP-1, CP-2, CP-4 and CP-10 represent the results for a device assembled according to the third example for 1, 2, 4 and 10 bilayers respectively. These results demonstrate that the efficiency and power efficiency and maximum luminance are all improved compared with the conventional device. The efficiency and the power efficiency are relatively insensitive to the number of bilayers of the conducting polymer of Figure 2 (e) and (f) in the range 1 to 10, however the maximum luminance is optimised with thin interfacial layers due to the increase in current density at a given drive voltage for thin interfacial layers.

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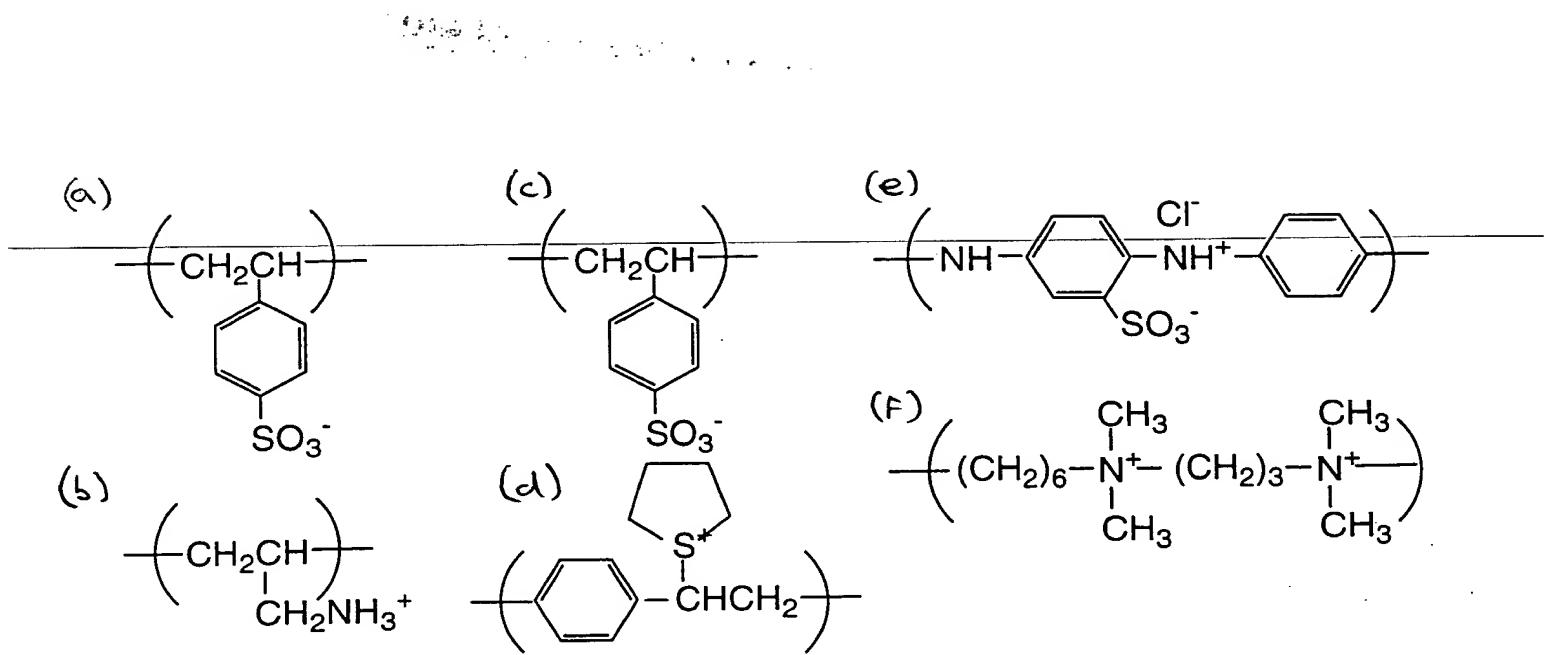
Fig. 1.



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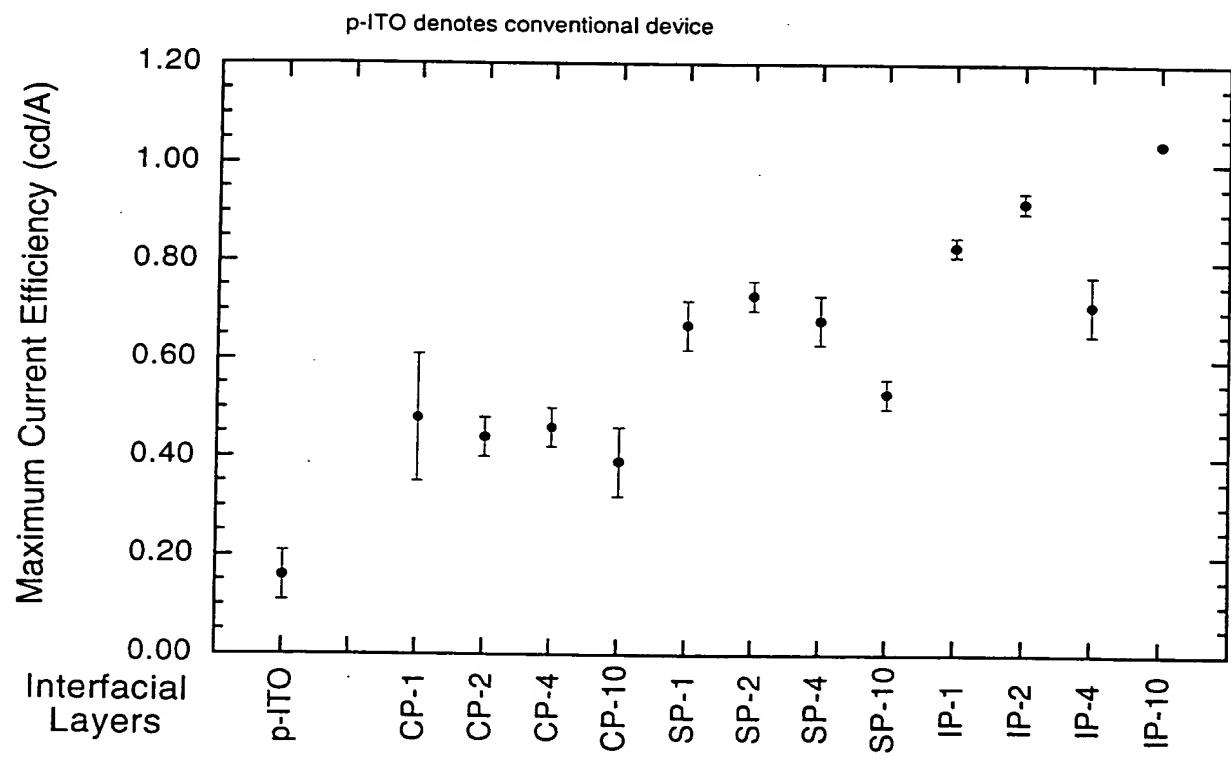
Fig. 2.



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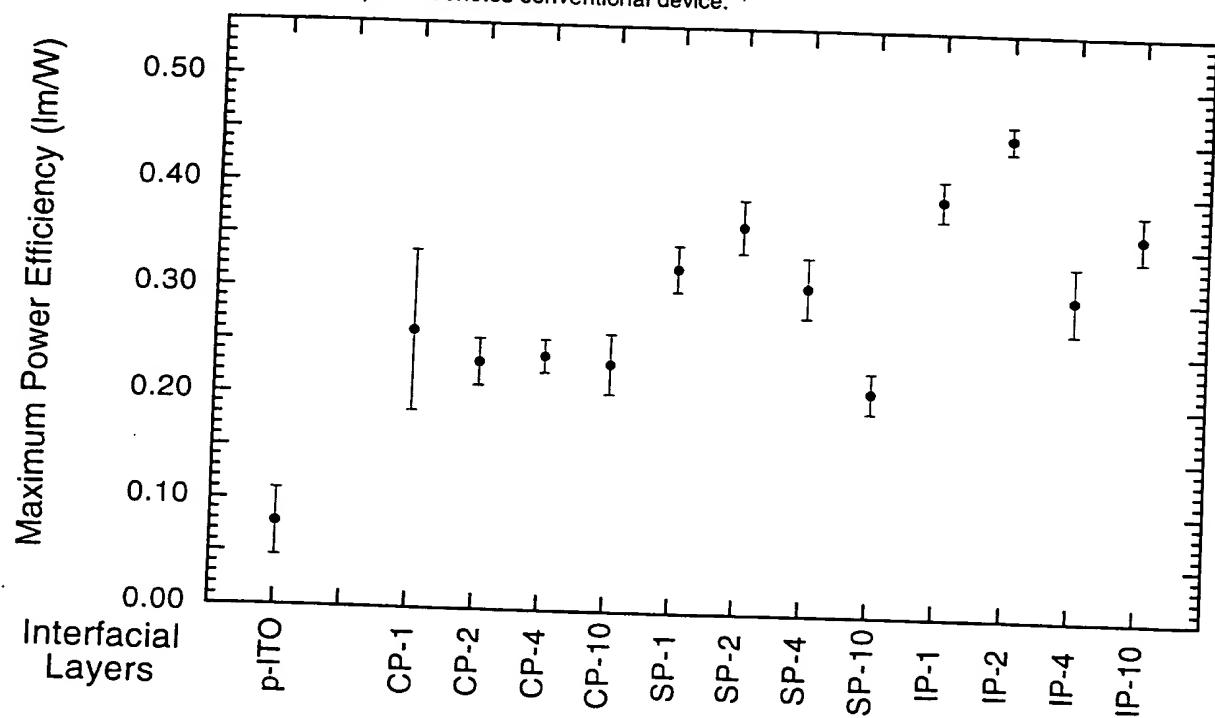
**Fig. 3. Maximum efficiency in cd/A**



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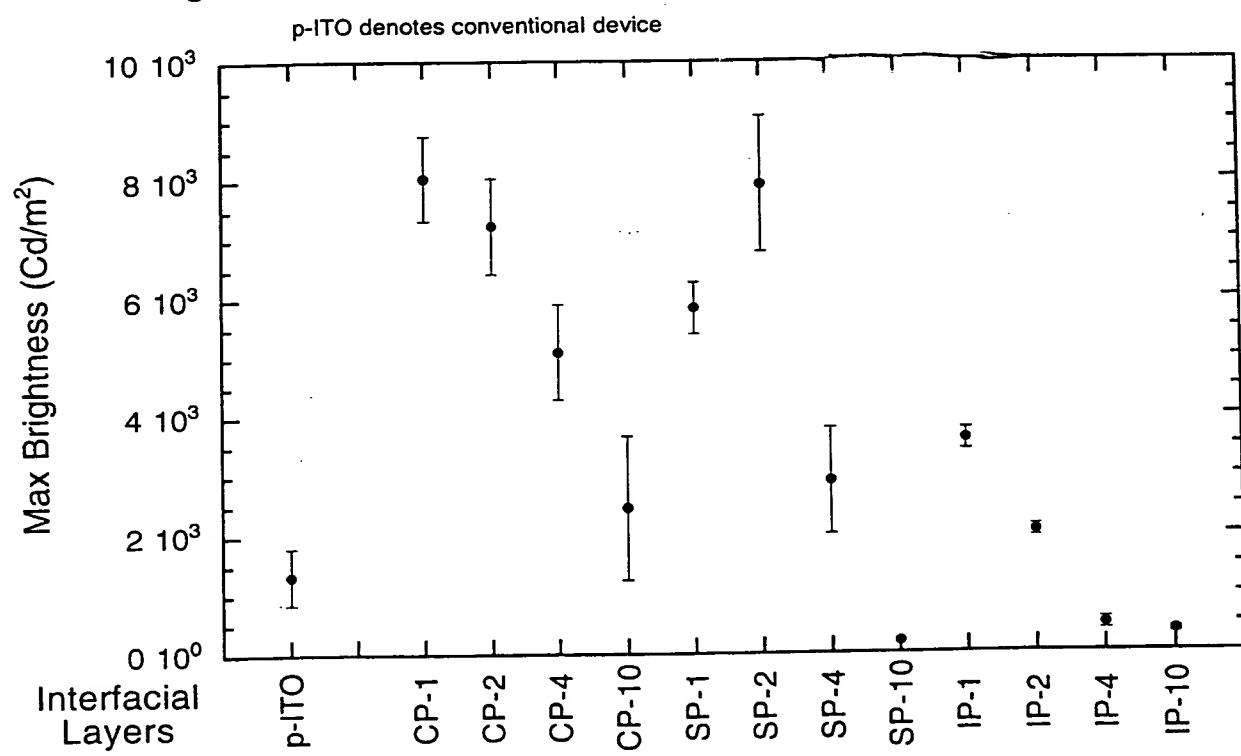
**Fig. 4. Maximum power efficiency (lm/W)**

p-ITO denotes conventional device.



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**Fig. 5. Maximum forward luminance under d.c. drive**



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